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㊹発明の名称　置換された1－アリール－5－(ヘト)アリールメチルアミノピラゾール類

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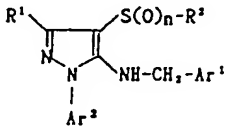
明　細　書

1　発明の名称

置換された1－アリール－5－(ヘト)アリールメチルアミノピラゾール類

2　特許請求の範囲

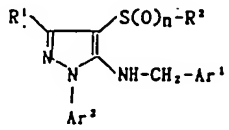
1．一般式(I)



(I)

式中、R^1は水素、アルキルまたはハロゲノアルキルを表わし、
R^2はアルキル、ハロゲノアルキル、随時置換されていてもよいアラルキルまたは随時置換されていてもよいアリールを表わし、
Ar^1は置換されたアリールまたは随時置換されていてもよいヘテロアリールを表わし、
Ar^2は各々の場合に随時置換されていてもよいフエニルまたはピリジルを表わし、そして
nは0、1または2の数を表わす、
の置換された1－アリール－5－(ヘト)アリールメチルアミノ－ピラゾール。

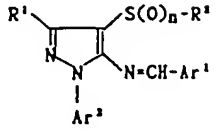
2．一般式(I)



(I)

式中、R^1は水素、アルキルまたはハロゲノアルキルを表わし、
R^2はアルキル、ハロゲノアルキル、随時置換されていてもよいアラルキルまたは随時置換されていてもよいアリールを表わし、
Ar^1は置換されたアリールまたは随時置換されていてもよいヘテロアリールを表わし、
Ar^2は各々の場合に随時置換されていてもよいフエニルまたはピリジルを表わし、そして
nは0、1または2の数を表わす、
の置換された1－アリール－5－(ヘト)アリー

ルメチルアミノーピラゾールを製造する際に、式（Ⅱ）



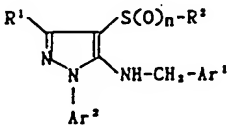
（Ⅱ）

式中、R^1、R^2、Ar^1、Ar^2及びnは上記の意味を有する、

の5－アラルキリデンイミノ－1－アリールピラゾール類を、適当ならば希釈剤の存在下で、還元剤と反応させることを特徴とする方法。

3．少なくとも1つの式（Ⅰ）の置換された1－アリール－5－（ヘト）アリールメチルアミノーピラゾールを含むことを特徴とする有害生物防除剤。

4．式（Ⅰ）の置換された1－アリール－5－（ヘト）アリールメチルアミノーピラゾールを、動物性有害生物及び／またはその環境に作用させることを特徴とする動物性有害生物の防除方法。



（Ⅰ）

式中、R^1は水素、アルキルまたはハロゲノアルキルを表わし、

R^2はアルキル、ハロゲノアルキル、随時置換されていてもよいアラルキルまたは随時置換されていてもよいアリールを表わし、

Ar^1は置換されたアリールまたは随時置換されていてもよいヘテロアリールを表わし、

Ar^2は各々の場合に随時置換されていてもよいフエニルまたはピリジルを表わし、そして

nは0、1または2の数を表わす、

の新規な置換された1－アリール－5－（ヘト）アリールメチルアミノーピラゾールが見い出された。

更に一般式（Ⅰ）

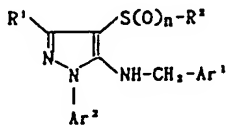
3　発明の詳細な説明

本発明は新規な置換された1－アリール－5－（メト）アリールメチルアミノーピラゾール、その製造方法、及びその有害生物防除剤（pest-combating agent）としての使用に関するものである。

ある1－アリールピラゾール例えば5－（N－メチルアミノ）－4－トリフルオロメチル－チオ－1－（2，6－ジクロロ－4－トリフルオロメチルフエニル）－ピラゾールまたは5－（N－メチルアミノ）－4－ジクロロフルオロメチルチオ－1－（2，6－ジクロロ－4－トリフルオロメチルフエニル）－ピラゾールが良好な殺虫作用を持つことは既に開示されている（ヨーロツパ特許第201,852号参照）。

しかしながら、これらの従来公知の化合物の活性は殊に低い施用割合及び濃度において有害な昆虫またはすべての施用分野に対して完全に満足できるものではない。

一般式（Ⅰ）



（Ⅰ）

式中、R^1は水素、アルキルまたはハロゲノアルキルを表わし、

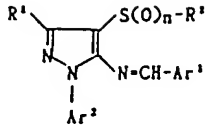
R^2はアルキル、ハロゲノアルキル、随時置換されていてもよいアラルキルまたは随時置換されていてもよいアリールを表わし、

Ar^1は置換されたアリールまたは随時置換されていてもよいヘテロアリールを表わし、

Ar^2は各々の場合に随時置換されていてもよいフエニルまたはピリジルを表わし、そして

nは0、1または2の数を表わす、

の新規な置換された1－アリール－5－（ヘト）アリールメチルアミノーピラゾールが式（Ⅱ）



(II)

式中、R^1、R^2、Ar^1、Ar^2及びnは上記の意味を有する、

の5－アラルキリデンイミノ－1－アリールピラゾールを適当ならば希釈剤の存在下で還元剤と反応させる場合に得られることが見い出された。

最後に、一般式（I）の新規な1－アリールピラゾールが良好な有害生物に対する作用を持つことが見い出された。

驚くべきことに、本発明による一般式（I）の置換された1－アリール－5－（ヘト）アリールメチルアミノ－ピラゾールは化学的及びその作用に関して類似の化合物である従来公知の1－アリールピラゾール例えば5－（N－メチルアミノ－4－トリフルオロメチルチオ）－1－（2，6－ジクロロ－4－トリフルオロメチルフェニル）－ピラゾールまたは5－（N－メチルアミノ－4－ジクロロフルオロメチルチオ）－1－（2，6－ジクロロ－4－トリフルオロメチルフェニル）－ピラゾールよりかなり良好な殺虫活性を示す。

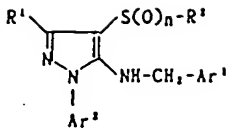
式（II）は本発明による置換された1－アリール－5－（ヘト）アリールメチルアミノ－ピラゾールの一般的定義を与える。好適な式（I）の化合物はR^1が水素或いは各々の場合に炭素原子1～4個及び適当ならば同一もしくは相異なるハロゲン原子1～9個を有する各々の場合に直鎖状もしくは分枝鎖状のアルキルまたはハロゲノアルキルを表わし、R^2が炭素原子1～8個を有する直鎖状もしくは分枝鎖状のアルキル、炭素原子1～8個及び同一もしくは相異なるハロゲン原子1～17個を有する直鎖状もしくは分枝鎖状のハロゲノアルキル、或いは適当ならば直鎖状もしくは分枝鎖状のアルキル部分中に炭素原子1～4個を有し、且つ随時同一もしくは相異なる置換基で1または多置換され、その際に各々の場合にフェニル部分中の適当な置換基にはハロゲン、シアノ、ニトロ、各々の場合に個々のアルキル部分中に炭素原子1～4個及び適当ならば同一もしくは相異なるハロゲン原子1～9個を有する各々の場合に直鎖状もしくは分枝鎖状のアルキル、アルコキシ、アルキルチオ、アルキルスルフィニル、アルキルスルホニル、ハロゲノアルキル、ハロゲノアルコキシ、ハロゲノアルキルチオ、ハロゲノアルキルスルフィニルまたはハロゲノアルキルスルホニルがあるフェニルアルキルまたはフェニルを表わし、Ar^1が同一もしくは相異なる置換基で1または多置換されるフェニル、或いは炭素原子1～9個及びヘテロ原子、殊に窒素、酸素または硫黄1～3個を有し、且つ随時同一もしくは相異なる置換基で1または多置換されていてもよいヘテロアリールを表わし、その際に各々の場合に適当な置換基にはR^2において挙げられたフェニル置換基があり、Ar^2が各々の場合に随時同一もしくは相異なる置換基で1または多置換されていてもよく、各々の場合に適当な置換基にはシアノ、ニトロ、ハロゲン、各々の場合に炭素原子1～4個を有する各々の場合に直鎖状もしくは分枝鎖状のアルキル、アルコキシまたはアルコキシカルボニル、各々の場合に炭素原子1～9個及び同一もしくは相異なるハロゲン原子1～9個を有する各々の場合に直鎖状もしくは分枝鎖状のハロゲノアルキルまたはハロゲノアルコキシ、或いは基 $-S(O)_p-R^3$ があるフェニル、2－ピリジル、3－ピリジルまたは4－ピリジルを表わし、ここにR^3がアミノ、並びにまた各々の場合に個々のアルキル部分中に炭素原子1～4個及びハロゲノアルキルの場合に同一もしくは相異なるハロゲン原子1～9個を有する各々の場合に直鎖状もしくは分枝鎖状のアルキル、アルキルアミノ、ジアルキルアミノまたはハロゲノアルキルを表わし、pが0、1または2の数を表わし、そしてnが0、1または2の数を表わすものである。

殊に好適な式（I）の化合物はR^1が水素、メチル、エチル、n－もしくはi－プロピルまたはトリフルオロメチルを表わし、R^2がメチル、エチル、n－もしくはi－プロピル、n－、i－、s－もしくはt－ブチル、n－もしくはi－ペン

チル、n－もしくはi－ヘキシル、クロロメチル、ジフルオロメチル、ジフルオロクロロメチル、フルオロジクロロメチル、トリフルオロメチル、ペンタフルオロエチル、ペンタクロロエチル、フルオロテトラクロロエチル、ジフルオロトリクロロエチル、トリフルオロジクロロエチル、テトラフルオロクロロエチル、ヘプタフルオロプロピル、クロロエチル、ブロモエチル、クロロプロピル、ブロモプロピル、ジクロロメチル、クロロフルオロメチル、トリクロロメチル、トリフルオロエチル、トリフルオロクロロエチル、テトラフルオロエチル、ジフルオロクロロエチル、フルオロジブロモエチル、ジフルオロブロモエチル、フルオロクロロブロモメチル、或いは各々の場合に随時同一もしくは相異なる置換基で1、2または3置換されていてもよく、各々の場合に適するフェニル置換基にはフツ素、塩素、臭素、ヨウ素、シアノ、ニトロ、メチル、エチル、メトキシ、メチルチオ、トリフルオロメチル、メチルスルフィニル、メチルスルホニル、トリフルオロメトキシ、トリフルオロメチルチオ、トリフルオロメチルスルフィニルまたはトリフルオロメチルスルホニルがあるフェニル、ベンジルまたはフェニルエチルを表わし、Ar^1が同一もしくは相異なる置換基で1、2または3置換されたフェニル或いは各々の場合に随時同一もしくは相異なる置換基で1、2または3置換されていてもよいピリジル、フリルまたはチエニルを表わし、その際に各々の場合に適当な置換基にはR^2において挙げられたフェニル置換基があり、Ar^2が随時同一もしくは相異なる置換基で1、2または3置換されていてもよいフェニル、または随時同一もしくは相異なる置換基で1、2または3置換されていてもよい2－ピリジルを表わし、その際に各々の場合に適当な置換基にはシアノ、ニトロ、フツ素、塩素、臭素、ヨウ素、メチル、エチル、n－及びi－プロピル、n－、i－、s－及びt－ブチル、メトキシ、エトキシ、メトキシカルボニル、エトキシカルボニル、トリフルオロメチル、トリクロロメチル、ジクロロフルオロメチル、ジフルオロクロロメチル、クロロメチル、ジクロロメチル、ジフルオロメチル、ペンタフルオロエチル、テトラフルオロエチル、トリフルオロクロロエチル、トリフルオロエチル、ジフルオロジクロロエチル、トリフルオロジクロロエチル、ペンタクロロエチル、トリフルオロメトキシ、トリクロロメトキシ、ジクロロフルオロメトキシ、ジフルオロクロロメトキシ、クロロメトキシ、ジクロロメトキシ、ジフルオロメトキシ、ペンタフルオロエトキシ、テトラフルオロエトキシ、トリフルオロクロロエトキシ、トリフルオロエトキシ、ジフルオロジクロロエトキシ、トリフルオロジクロロエトキシ、ペンタクロロエトキシまたは基 $-S(O)_p-R^3$ があり、ここにR^3がアミノ、メチルアミノ、エチルアミノ、ジメチルアミノ、ジエチルアミノ、フルオロジクロロメチル、ジフルオロメチル、テトラフルオロエチル、トリフルオロクロロエチル、トリクロロメチル、トリクロロエチル、トリフルオロメチル、メチルまたはエチルを表わし、pが0、1または2の数を表わし、そしてnが0、1または2の数を表わすものである。

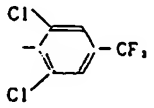
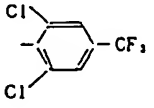
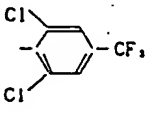
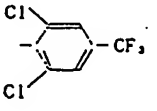
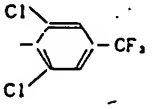
極めて殊に好適な式（I）の化合物はR^1が水素またはメチルを表わし、R^2がメチル、エチル、トリフルオロメチル、ジクロロフルオロメチルまたはクロロジフルオロメチルを表わし、Ar^1が随時同一もしくは相異なる置換基で1、2または3置換され、その際に適当な置換基にはフツ素、塩素、臭素、メチルまたはトリフルオロメチルがあるフェニルまたはピリジルを表わし、Ar^2が随時同一もしくは相異なる置換基で1～5置換され、その際に適当な置換基にはフツ素、塩素、臭素、メチル、エチル、メトキシ、エトキシ、トリフルオロメチル、トリフルオロメトキシ、トリフルオロメチルチオ、トリフルオロメチルスルフィニルまたはトリフルオロメチルスルホニルがあるフェニルを表わし、そしてnが0、1または2の数を表わすものである。

製造実施例に挙げられる化合物に加えて次の一般式（I）

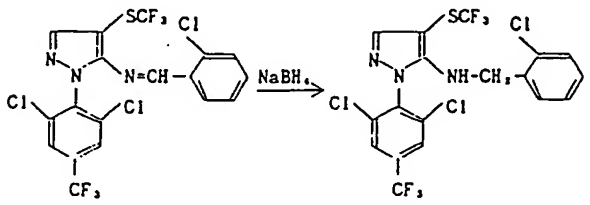


（Ⅰ）

の置換された１－アリール－５－（ヘト）アリールメチルアミノ－ピラゾールを個々に挙げ得る：

R^1	$-S(O)n-R^2$	Ar^1	Ar^2
H	$SCCl_2F$		
H	$SCClF_2$		
CH_3	SCF_3		
H	SCF_3		
CH_3	SCF_3		

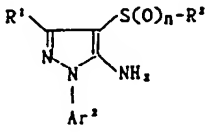
出発物質として例えば５－［Ｎ－（２－クロロベンジリデン）－イミノ］－４－トリフルオロメチルチオ－１－（２，６－ジクロロ－４－トリフルオロメチルフェニル）－ピラゾール及び還元剤として水素化ホウ素ナトリウムを用いる場合、本発明による工程の反応の径路は次式により表わし得る：



式（Ⅱ）は本発明による工程を行う際に出発物質として必要とされる５－アラルキリデンイミノ－１－アリールピラゾールの一般的定義を与える。この式（Ⅱ）において、R^1、R^2、Ar^1、Ar^2及びｎは好ましくは本発明による式（Ⅰ）の物質の記載に関連してこれらの置換基に対して好適なものとして既に挙げられたものの基を表わす。

式（Ⅱ）の５－アラルキリデンイミノ－１－アリールピラゾールは従来未知であつた。しかしながら、これらのものは本出願社による関連した特許出願の目的である。

これらのものは式（Ⅲ）



（Ⅲ）

式中、R^1、R^2、Ar^2及びｎは上記の意味を有する、

の５－アミノ－１－アリールピラゾールを適当ならば希釈剤例えばトルエンの存在下及び適当ならば反応補助剤例えば硫酸の存在下にて０乃至１２０℃間の温度で式（Ⅳ）

$$Ar^1-CHO \qquad (Ⅳ)$$

式中、Ar^1は上記の意味を有する、

のアルデヒドと反応させる場合に得られる。

式（Ⅲ）の5－アミノー1－アリールピラゾールは公知であるか、または公知の方法と同様に得ることができる（ヨーロッパ特許第201,852号参照）。

本発明による工程を行うに適する還元剤にはかかる還元反応に通常であるすべての還元剤がある。複合水素化物例えば水素化ホウ素ナトリウム、水素化シアノホウ素ナトリウム、水素化ホウ素リチウムまたは水素化リチウムアルミニウムを好適に用いる。

用いる還元剤に依存して、本発明による工程を行うに適する希釈剤にはすべての通常の有機または無機溶媒がある。エーテル例えばジエチルエーテル、ジオキサンもしくはテトラヒドロフランまたはアルコール例えばメタノール、エタノールもしくはプロパノールを好適に用いる。

本発明による工程を行う際に、反応温度は用いる還元剤に依存して比較的広い範囲内で変え得る。一般に、反応は－20乃至150℃間の温度、好ましくは0乃至120℃間の温度で行う。

本発明による工程を行う場合、式（Ⅱ）の5－アラルキリデンイミノー1－アリールピラゾール1モル当り0.25～5.0モル、好ましく0.25～2.0モルの還元剤を一般に用いる。反応を行い、そして一般的に通常の方法により反応生成物を処理し、そして単離する。

本活性化合物は農業、林業、貯蔵製品及び材料の保護、並びに衛生分野において遭遇する動物性有害生物、殊に昆虫、クモ（arachnida)及び線虫（nematode)を防除する際に適しており、そして良好な植物許容性及び温血動物に対する好ましい毒性を有している。

それらは通常の感受性の及び抵抗性の種及び全てのまたはある成長段階に対して活性である。

上記した有害生物には、次のものが包含される：等脚目(Isopoda)のもの、例えばオニスカス・アセルス(Oniscus asellus)、オカダンゴムシ(Armadillidium vulgare)、及びポルセリオ・スカバー(Porcellio scabar)。倍脚綱(Diplopoda)のもの、例えば、ブラニウルス・グットラタス(Blaniulus guttulatus)。チロポダ目(Chilopoda)のもの、例えば、ゲオフイルス・カルポファグス(Geophilus carpohagus)及びスカチゲラ(Scutigera spp.)。シムフイラ目(Symphyla)のもの、例えばスカチゲレラ・イマキュラタ(Scutigerella immaculata)。シミ目(Thysanura)のもの、例えばレプシマ・サッカリナ(Lepisma saccharina)。トビムシ目(Collembola)のもの、例えばオニチウルス・アルマツス(Onychiurus armatus)。直翅目(Orthoptera)のもの、例えばブラッタ・オリエンタリス(Blatta orientalis)、ワモンゴキブリ(Periplaneta americana)、ロイコファエ・マデラエ(Leucophaea maderae)、チャバネ・ゴキブリ(Blattella germanica)、アチータ・ドメスチクス(Acheta domesticus)、ケラ(Gryllotalpa spp.)、トノサマバッタ(Locusta migratoria migratorioides)、メラノプルス・ジフエレンチアリス(Melanoplusdifferentialis)及びシストセルカ・グレガリア(Schistocerca gregaria)。ハサミムシ目(Dermaptere)のもの、例えばホルフイキュラ・アウリクラリア(Forficula auricularia)。シロアリ目(Isoptera)のもの、例えばレチキュリテルメス(Reticulitermes spp.)。シラミ目(Anoplura)のもの、例えばフイロクセラ・バスタリクス(Phylloxera vastatrix)、ペンフイグス(Pemphigus spp.)、及びヒトジラミ(Pediculus humanus corporis)、ケモノジラミ(Haematopinus spp.)及びケモノホソジラミ(Linognathus spp.)。ハジラミ目(Mallophaga)のもの、例えばケモノハジラミ(Trichodectes spp.)及びダマリネア(Damalinea spp.)。アザミウマ目(Thysanoptera)のもの、例えばクリバネアザミウマ(Hercinothrips femoralis) 及びネギアザミウマ(Thrips tabaci)。半翅目(Heteroptera)のもの、例えばチャイロカメムシ(Eurygaster spp.)、ジスデルクス・インテルメジウス(Dysdercus intermedius)、ピエスマ・クワドラタ(Piesma quadrata)、ナンキンムシ(Cimex lectularius)、ロド

ニウス・プロリクス(Rhodnius prolixus)及びトリアトマ(Triatoma spp.)。同翅目(Homoptera)のもの、例えばアレウロデス・ブラシカエ(Aleurodes brassicae)、ワタコナジラミ(Bemisia tabaci)、トリアレウロデス・バポラリオルム(Trialeurodes vaporariorum)、ワタアブラムシ(Aphis gossypii)、ダイコンアブラムシ(Brevicoryne brassicae)、クリプトミズス・リビス(Cryptomyzus ribis)、ドラリス・ファバエ(Doralis fabae)、ドラリス・ポミ(Doralis pomi)、リンゴワタムシ(Eriosoma lanigerum)、モモコフキアブラムシ(Hyaloperus arundinis)、ムギヒゲナガアブラムシ(Macrosiphumavenae)、コブアブラムシ(Myzus spp.)、ホップイボアブラムシ(Phorodon humuli)、ムギクビレアブラムシ(Rhopalosiphum padi)、ヒメヨコバイ(Empoasca spp.)、ユースセリス・ビロバツス(Euscelis bilobatus)、ツマグロヨコバイ(Nephotettix cincticeps)、ミズキカタカイガラムシ(Lecanium corni)、オリーブカタカイガラムシ(Saissetia oleae)、ヒメトビウンカ(Laodelphax striatellus)、トビイロウンカ(Nilaparvata lugens)、アカマルカイガラムシ(Aonidiella aurantii)、シロマルカイガラムシ(Aspidiotus hederae)、プシユードコツカス(Pseudococcus spp.)及びキジラミ(Psylla spp.)。鱗翅目(Lepidoptera)のもの、例えばワタアカミムシ(Pectinophora gossypiella)、ブパルス・ピニアリウス(Bupalus piniarius)、ケイマトビア・ブルマタ(Cheimatobia brumata)、リソコレチス・ブランカルデラ(Lithocol letisblancardella)、ヒポノミユウタ・パデラ(Hyponomeuta padella)、コナガ(Plutella maculipennis)、ウメケムシ(Malacosoma neustria)、クワノキンムケシ(Euproctis chrysorrhoea)、マイマイガ(Lyman·tria spp.)、ブツカラトリックス・スルベリエラ(Bucculatrix thurberiella)、ミカンハモグリガ(Phyllocnistis citrella)、ヤガ(Agrotis spp.)、ユークソア(Euxoa spp.)、フエルチア(Feltia spp.)、エアリアス・インスラナ(Earias insulana)、ヘリオチス(Heliothis spp.)、ヒロイチモジヨトウ(Laphygma exigua)、ヨトウムシ(Mamestra brassicae)、パノリス・フラメア(Panolis flammea)、ハスモンヨトウ(Prodenia litura)、シロナヨトウ(Spodoptera spp.)、トリコプルシア・ニ(Trichoplusia ni)、カルポカプサ・ポモネラ(Carpocapsa pomonella)、アオムシ(Pieris spp.)、ニカメイチユウ(Chils spp.)、アワノメイガ(Pyrausta nubilalis)、スジコナマダラメイガ(Ephestia kuehniella)、ハチミツガ(Galleria mellonella)、テイネオラ・ビセリエラ(Tineola bisselliella)、テイネア・ペリオネラ(Tinea pellionella)、ホフマノフイラ・プシユードスプレテラ(Hofmannophila pseudospretella)、カコエシア・ポダナ(Cacoecia podana)、カプア・レチクラナ(Capua reticulana)、クリストネウラ・フミフエラナ(Choristoneura fumiferana)、クリシア・アンビグエラ(Clysia ambiguella)、チヤハマキ(Homona magnanima)、及びトルトリクス・ビリダナ(Tortrix viridana)。鞘翅目(Coleoptera)のもの、例えばアノビウム・プンクタツム(Anobium punctatum)、コナナガシンクイムシ(Rhizopertha dominica)、ブルキジウス・オブテクツス(Bruchidius obtectus)、インゲンマメゾウムシ(Acanthoscelides obtectus)、ヒロトルペス・バジユルス(Hylotrupes bajulus)、アゲラスチカ・アルニ(Agelastica alni)、レプチノタルサ・デセムリネアタ(Leptinotarsa decemlineata)、フエドン・コクレアリアエ(Phaedon cochleariae)、ジアブロチカ(Diabrotica spp.)、プシリオデス・クリソセファラ(Psylliodes chrysocephala)、ニジユウヤホシテントウ(Epilachna varivestis)、アトマリア(Atomaria spp.)、ノコギリヒラタムシ(Oryzaephilus surinamensis)、ハナゾウムシ(Anthonomus spp.)、コクゾウムシ(Sitophilus spp.)、オチオリンクス・スルカツス(Otiorrhychus sulcatus)、バシヨウゾウムシ(Cos

mopolites sordidus)、シユートリンクス・アシミリス(Ceuthorrhynchus assimillis)、ヒペラ・ポスチカ(Hypera postica)、カツオブシムシ(Dermestes spp.)、トロゴデルマ(Trogoderma spp.)、アントレヌス(Anthrenus spp.)、アタゲヌス(Attagenus spp.)、ヒラタキクイムシ(Lyctus spp.)、メリゲテス・アエネウス(Meligethes aeneus)、ヒヨウホンムシ(Ptinus spp.)、ニプツス・ホロレウカス(Niptus hololeucus)、セマルヒヨウホンムシ(Gibbium psylloides)、コクヌストモドキ(Tribolium spp.)、チャイロコメノゴミムシダマシ(Tenebrio molitor)、コメツキムシ(Agriotes spp.)、コノデルス(Conoderus spp.)、メロロンサ・メロロンサ(Melolontha melolontha)、アムフィマロン・ソルスチチアリス(Amphimallonsolstitialis)及びコステリトラ・ゼアランジカ(Costelytra zealandica)。膜翅目(Hymenoptera)のもの、例えばマツハバチ(Diprion spp.)、ホプロカムパ(Hoplocampa spp.)、ラシウス(Lasius spp.)、イエヒメアリ(Monomorium pharaonis)及びスズメバチ(Vespa spp.)。双翅目(Diptera)のもの、例えばヤブカ(Aedes spp.)、ハマダラカ(Anopheles spp.)、イエカ(Culex spp.)、キイロショウジョウバエ(Drosophila melanogaster)、イエバエ(Musca spp.)、ヒメイエバエ(Fannia spp.)、クロバエ・エリスロセファラ(Calliphoro erythrocephala)、キンバエ(Lucilia spp.)、オビキンバエ(Chrysomya spp.)、クテレブラ(Cuterebra spp.)、ウマバエ(Gastrophilus spp.)、ヒツポボスカ(Hyppobosca spp.)、サシバエ(Stomoxys spp.)、ヒツジバエ(Oestrus spp.)、ウシバエ(Hypoderma spp.)、アブ(Tabanus spp.)、タニア(Tannia spp.)、ケバエ(Bibio hortulanus)、オスシネラ・フリト(Oscinella frit)、クロキンバエ(Phorbia spp.)、アカザモグリハナバエ(Pegomyia hyoscyami)、セラチチス・キヤピタータ(Ceratitis capitata)、ミバエオレアエ(Dacus oleae)及びガガンボ・パルドーサ(Tipula paludosa)。ノミ目(Siphonaptera)のもの、例えばケオプスネズミノミ(Xenopsylla cheopis)及びナガノミ(Ceratopyllus spp.)。

本発明による活性化合物は強い殺虫作用に特徴がある。これらのものは植物に対して有害である昆虫例えばマスタード・ビートル(Phaedon cochleariae)の幼虫(Aphis fabae)に対して殊に良好に使用し得る。

加えてまた、本発明による活性化合物は土壌昆虫を防除する際に適しており、そして例えば土壌虫のオニオン・フライの幼虫(Pharbia antiqua)を防除する際に使用し得る。

加えて、本発明による活性化合物は衛生上の有害生物及び貯蔵製品の有害生物に対して高い活性を有する。

本活性化合物は普通の組成物例えば、溶液、乳液、懸濁剤、粉末、包沫剤、塗布剤、水和剤、顆粒、エアロゾル、活性化合物を含浸させた天然及び合成物質、種子用の重合物質中の極く細かいカプセル及びコーテイング組成物、燃焼装置に用いる組成物、例えばくん蒸カートリッジ、くん蒸カン及びくん蒸コイル等、並びにULV冷ミスト及び温ミスト組成物に変えることができる。

これらの組成物は公知の方法において、例えば活性化合物を伸展剤、即ち液体溶媒及び/または固体の担体と随時表面活性剤、即ち乳化剤及び/または分散剤及び/または発泡剤と混合して製造される。また伸展剤として水を用いる場合、例えば補助溶媒として有機溶媒を用いることもできる。液体溶媒として、主に、芳香族炭化水素例えばキシレン、トルエンもしくはアルキルナフタレン、塩素化された芳香族もしくは塩素化された脂肪族炭化水素例えばクロロベンゼン、クロロエチレンもしくは塩化メチレン、脂肪族炭化水素例えばシクロヘキサン、またはパラフイン例えば鉱油留分、鉱油及び植物油、アルコール例えばブタノールもしくはグリコール並びにそのエーテル及びエステル、ケトン例えばアセトン、メチルエチルケトン、メチルイソブチルケトンもしくはシクロヘキサノン、強い有極性溶媒例えばジメチルホルムアミド

(19) The Japanese Patent Office (JP)
(12) Japanese Patent Laid-Open Bulletin (A)
(11) Patent Application Laid-Open No. Syou-64-47768
(43) Date of laid-open: February 22, 1989
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C07D 231/44		6529-4C
A01N 43/56		D-7215-4H
C07D 401/12	231	6761-4C

Request for examination: not yet filed
Number of claims: 4
(total 15 pages)

(54) Title of the Invention: Substituted 1-aryl-5-(het)arylmethylaminopyrazoles

(21) Japanese Patent Application No. Syou-63-182841
(22) Filing Date of Application: July 23, 1988
Priority claimed (32) July 28, 1987 (33) West Germany (DE)
(31) P3724920.7

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To be continued to final page

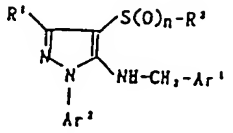
SPECIFICATION

1. Title of the Invention

Substituted 1-aryl-5-(het)arylmethylaminopyrazoles

2. Claims

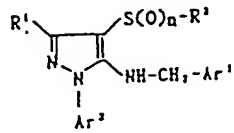
1. A substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



(I)

wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,
Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,
Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and
n represents one number of 0, 1 or 2.

2. A process for producing a substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



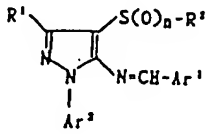
(I)

wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,

Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,

Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and

n represents one number of 0, 1 or 2, wherein a 5-aralkylideneimino-1-arylpyrazole of the formula (II):



(II)

wherein R^1, R^2, Ar^1, Ar^2 and n have the above-described meanings,

is reacted with a reducing agent, if appropriate, in the presence of a diluent.

3. A pest-combating agent comprising at least one substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I).

4. A method for combating an animal pest, wherein the animal pest and/or an environment thereof is treated with an substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I).

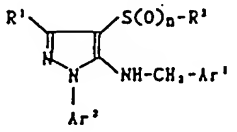
3. Detailed Description of the Invention

The present invention relates to a novel substituted 1-aryl-5-(het)arylmethylaminopyrazole, a process for producing the same, and a use thereof as a pest-combating agent.

It has already been disclosed that some 1-arylpyrazole, for example, 5-(N-methylamino)-4-trifluoromethylthio-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole or 5-(N-methylamino)-4-dichlorofluoromethylthio-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole has a good insecticidal activity (cf. European patent No. 201,852).

However, the activity of these hitherto known compounds is not completely satisfactory against harmful insects or all the application fields especially at a low application rate and concentration.

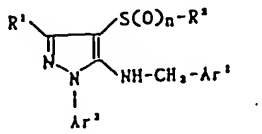
There has been found a novel substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



(I)

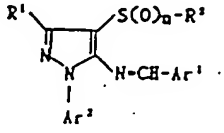
wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,
Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,
Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and
n represents one number of 0, 1 or 2.

Furthermore, it was found that a novel substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



(I)

wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,
Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,
Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and
n represents one number of 0, 1 or 2,
is obtained by reacting a 5-aralkylideneimino-1-arylpyrazole of the formula (II):



(II)

wherein R^1, R^2, Ar^1, Ar^2 and n have the above-described meanings,
with a reducing agent, if appropriate, in the presence of a diluent.

Finally, it has been found that the novel 1-arylpyrazole of the general formula (I) has a good action against pests.

Surprisingly, the substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I) according to the invention exhibits a considerably better insecticidal activity than the known 1-arylpyrazole which is a chemically and actionally analogous compound, for example, 5-(N-methylamino-4-trifluoromethylthio-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole or 5-(N-methylamino-4-dichlorofluoromethylthio)-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole.

The formula (I) affords a general definition of the substituted 1-aryl-5-(het)arylmethylaminopyrazole according to the invention. Preferred compound of the formula (I) is a compound wherein R^1 represents hydrogen or, in each case, linear or branched alkyl or halogenoalkyl, in each case, having 1 to 4 carbon atoms and, if appropriate, 1 to 9, the same or different, halogen atoms; R^2 represents linear or branched alkyl having 1 to 8 carbon atoms, linear or branched halogenoalkyl having 1 to 8 carbon atoms and 1 to 17, the same or different, halogen atoms, or phenylalkyl or phenyl having, if appropriate, 1 to 4 carbon atoms in the linear or branched alkyl part and optionally monosubstituted or polysubstituted with the same or different substituent(s),

wherein, in each case, appropriate substituents in the phenyl part include halogen, cyano, nitro, or, in each case, a linear or branched alkyl, alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyl, halogenoalkyl, halogenoalkoxy, halogenoalkylthio, halogenoalkylsulfinyl or halogenoalkylsulfonyl, in each case, having 1 to 4 carbon atoms and, if appropriate, 1 to 9, the same or different, halogen atoms in the individual alkyl part; Ar^1 represents phenyl monosubstituted or polysubstituted with the same or different substituent(s), or heteroaryl having 1 to 9 carbon atoms and hetero atom(s), especially 1 to 3 nitrogens, oxygens or sulfurs and optionally monosubstituted or polysubstituted with the same or different substituent(s), wherein appropriate substituents in each case include the phenyl substituents as described for R^2; Ar^2 represents phenyl, 2-pyridyl, 3-pyridyl or 4-pyridyl, in each case, optionally monosubstituted or polysubstituted with the same or different substituent(s), wherein appropriate substituents in each case include cyano, nitro, halogen, or, in each case, linear or branched alkyl, alkoxy, or alkoxycarbonyl, in each case, having 1 to 4 carbon atoms, or, in each case, linear or branched halogenoalkyl or halogenoalkoxy, in each case, having 1 to 9 carbon atoms and 1 to 9, the same or different, halogen atoms, or a group $-S(O)_p-R^3$, wherein R^3

represents amino or, in each case, alkyl, alkylamino, dialkylamino or halogenoalkyl, in each case, having 1 to 4 carbon atoms in the individual alkyl part and, in the case of halogenoalkyl, having 1 to 9, the same or different, halogen atoms; p represents one number of 0, 1 or 2; and n represents one number of 0, 1 or 2.

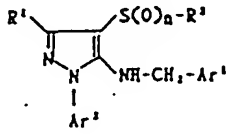
Particularly preferred compound of the formula (I) is a compound wherein R^1 represents hydrogen, methyl, ethyl, n- or i-propyl or trifluoromethyl, R^2 represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n- or i-pentyl, n- or i-hexyl, chloromethyl, difluoromethyl, difluorochloromethyl, fluorodichloromethyl, trifluoromethyl, pentafluoroethyl, pentachloroethyl, fluorotetrachloroethyl, difluorotrichloroethyl, trifluorodichloroethyl, tetrafluorochloroethyl, heptafluoropropyl, chloroethyl, bromoethyl, chloropropyl, bromopropyl, dichloromethyl, chlorofluoromethyl, trichloromethyl, trifluoroethyl, trifluorochloroethyl, tetrafluoroethyl, difluorochloroethyl, fluorodibromoethyl, difluorobromoethyl, fluorochlorobromomethyl, or phenyl, benzyl or phenylethyl, in each case, optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents on phenyl in each case include fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, methoxy,

methylthio, trifluoromethyl, methylsulfinyl, methylsulfonyl, trifluoromethoxy, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl; Ar^1 represents phenyl monosubstituted, disubstituted or trisubstituted with the same or different substituent(s) or pyridyl, furyl or thienyl, in each case, optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents in each case include the phenyl substituents described for R^2; Ar^2 represents phenyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s) or 2-pyridyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents in each case include cyano, nitro, fluoro, chloro, bromo, iodo, methyl, ethyl, n- and i-propyl, n-, i-, s- and t-butyl, methoxy, ethoxy, methoxycarbonyl, ethoxycarbonyl, trifluoromethyl, trichloromethyl, dichlorofluoromethyl, difluorochloromethyl, chloromethyl, dichloromethyl, difluoromethyl, pentafluoroethyl, tetrafluoroethyl, trifluorochloroethyl, trifluoroethyl, difluorodichloroethyl, trifluorodichloroethyl, pentachloroethyl, trifluoromethoxy, trichloromethoxy, dichlorofluoromethoxy, difluorochloromethoxy, chloromethoxy, dichloromethoxy, difluoromethoxy,

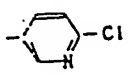
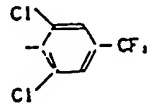
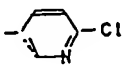
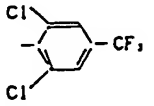
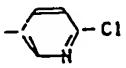
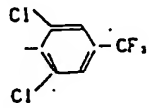
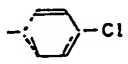
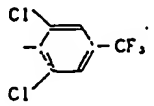
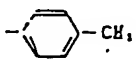
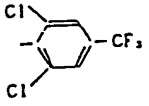
pentafluoroethoxy, tetrafluoroethoxy, trifluorochloroethoxy, trifluoroethoxy, difluorodichloroethoxy, trifluorodichloroethoxy, pentachloroethoxy or a group $-S(O)_p-R^3$, wherein R^3 represents amino, methylamino, ethylamino, dimethylamino, diethylamino, fluorodichloromethyl, difluoromethyl, tetrafluoroethyl, trifluorochloroethyl, trichloromethyl, trichloroethyl, trifluoromethyl, methyl or ethyl; p represents one number of 0, 1 or 2; and n represents one number of 0, 1 or 2.

Very particularly preferred compound of the formula (I) is a compound wherein R^1 represents hydrogen or methyl; R^2 represents methyl, ethyl, trifluoromethyl, dichlorofluoromethyl or chlorodifluoromethyl; Ar^1 represents phenyl or pyridyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents include fluoro, chloro, bromo, methyl or trifluoromethyl; Ar^2 represents phenyl optionally monosubstituted to pentasubstituted with the same or different substituent(s), wherein appropriate substituents include fluoro, chloro, bromo, methyl, ethyl, methoxy, ethoxy, trifluoromethyl, trifluoromethoxy, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl and n represents one number of 0, 1 or 2.

In addition to the compounds described in Production Examples, the following substituted 1-aryl-5-(het)arylmethylamino-pyrazoles of the general formula (I) may be individually mentioned.

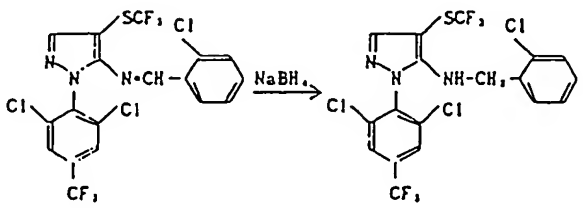


(I)

R^1	$-S(O)_n-R^2$	Ar^1	Ar^2
H	$SCCl_2F$		
H	$SCCl_2F$		
CH_3	SCF_3		
H	SCF_3		
CH_3	SCF_3		

In the case that, for example, 5-[N-(2-chlorobenzylidene)-imino]-4-trifluoromethylthio-1-(2,6-dichloro-4-trifluoromethylphenyl)-pyrazole is used as a

starting material and sodium borohydride as a reducing agent, the reaction pathway of the process according to the invention may be shown by the following scheme:

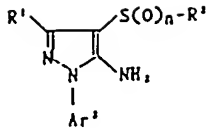


The formula (II) affords a general definition of 5-aralkylideneimino-1-arylpyrazole necessary as a starting material for carrying out the process according to the invention.

In the formula (II), R^1, R^2, Ar^1, Ar^2 and n preferably represent the groups already mentioned as preferable groups for these substituents with regard to the substance of the formula (I) according to the invention.

The 5-aralkylideneimino-1-aryl-pyrazole of the formula (II) is hitherto unknown. However, the compound is objective of the related patent application submitted by the present applicant.

The compound is obtained by reacting a 5-amino-1-aryl-pyrazole of the formula (III),



(III)

wherein R^1, R^2, Ar^2 and n have the meanings as above, with an aldehyde of the formula (IV):

Ar^1-CHO (IV)

wherein Ar^1 has the meaning as above,
at a temperature between 0 and 120 °C, if appropriate, in the presence of a diluent such as toluene and, if appropriate, in the presence of a reaction auxiliary agent such as sulfuric acid.

The 5-amino-1-aryl-pyrazole of the formula (III) is known or obtainable in a similar manner to the known method (cf. European Patent No. 201,852).

The reducing agent suitable for carrying out the process according to the invention includes all the reducing agents common for such a reduction reaction. Preferably used is a complex hydride, for example, sodium borohydride, sodium cyanoborohydride, lithium borohydride or lithium aluminum hydride.

Depending on the reducing agent used, the diluent suitable for carrying out the process according to the

invention includes all the common organic or inorganic solvents. Preferably used is an ether, such as diethyl ether, dioxane or tetrahydrofuran, or an alcohol, such as methanol, ethanol or propanol.

At carrying out the process according to the invention, the reaction temperature may be varied within a relatively wide range depending on the reducing agent used. Generally, the reaction is carried out at a temperature between -20 and 150°C, preferably at a temperature between 0 and 120°C.

In the case of carrying out the process according to the invention, the reducing agent is generally used in an amount of 0.25 to 5.0 mol, preferably 0.25 to 2.0 mol per 1 mol of 5-aralkylideneimino-1-aryl-pyrazole of the formula (II). The reaction is carried out, and the reaction product is generally treated in a usual manner and then isolated.

The active compounds are suitable for combating animal pests, in particular insects, arachnids and nematodes, which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field and are well tolerated by plants and have a preferable toxicity towards warm-blooded animals.

They are active against normally sensitive and resistant specie and against all or some stages of development.

The above-mentioned pests include the following: Those belonging to the order of the Isopoda, for example, Oniscus asellus, Armadillidium vulgare and Porcellio scabar. Those belonging to the order of the Diplopoda, for example, Blaniulus guttulatus. Those belonging to the order of the Chilopoda, for example, Geophilus carpohagus and Scutigera spp. Those belonging to the order of the Symphyla, for example, Scutigerella immaculata. Those belonging to the order of the Thysanura, for example, Lepisma saccharina. Those belonging to the order of the Collembola, for example, Onychiurus armatus. Those belonging to the order of the Orthoptera, for example, Blatta orientalis, Periplaneta americana, Leucophaea maderae, Blattella germanica, Acheta domesticus, Gryllotalpa spp., Locusta migratoria migratorioides, Melanoplus differentialis and Schistocerca gregaria. Those belonging to the order of the Dermaptera, for example, Forficula auricularia. Those belonging to the order of the Isoptera, for example, Reticulitermes spp. Those belonging to the order of the Anoplura, for example, Phylloxera vastatrix, Pemphigus spp., Pediculus humanus corporis, Haematopinus spp. and Linognathus spp. Those

belonging to the order of the Mallophaga, for example, Trichodectes spp. and Damalinea spp. Those belonging to the order of the Thysanoptera, for example, Hercinothrips femoralis and Thrips tabaci. Those belonging to the order of the Heteroptera, for example, Eurygaster spp.,Dysdercus intermedius, Piesma quadrata, Cimex lectularius, Rhodnius prolixus and Triatoma spp. Those belonging to the order of the Homoptera, for example, Aleurodes brassicae, Bemisia tabaci, Trialeurodes vaporariorum, Aphis gossypii, Brevicoryne brassicae, Cryptomyzus, ribis, Doralis fabae, Doralis pomi, Eriosoma lanigerum, Hyalopterus arundinis, Macrosiphum avenae, Myzus spp., Phorodon humuli, Rhopalosiphum padi, Empoasca spp., Euscelis bilobatus, Nephotettix cincticeps, Lecanium corni, Saissetia oleae, Laodelphax striatellus, Nilaparvata lugens, Aonidiella aurantii, Aspidiotus hederae, Pseudococcus spp. and Psylla spp. Those belonging to the order of the Lepidoptera, for example, Pectinophora gossypiella, Bupalus piniarius, Cheimatobia brumata, Lithocolletis blancardella, Hyponomeuta padella, Plutella maculipennis, Malacosoma neustria, Euproctis chrysorrhoea, Lymantria spp. Bucculatrix thurberiella, Phyllocnistis citrella, Agrotis spp., Euxoa spp., Feltia spp., Earias insulana, Heliothis spp., Laphygma exigua, Mamestra brassicae, Panolis flammea, Prodenia litura, Spodoptera spp., Trichoplusia ni,

Carpocapsa pomonella, Pieris spp., Chilo spp., Pyrausta nubilalis, Ephestia kuehniella, Galleria mellonella, Tineola bisselliella, Tinea pellionella, Hofmannophila pseudospretella, Cacoecia podana, Capua reticulana, Choristoneura fumiferana, Clysia ambiguella, Homona magnanima and Tortrix viridana. Those belonging to the order of the Coleoptera, for example, Anobium punctatum, Rhizopertha dominica, Bruchidius obtectus, Acanthoscelides obtectus, Hylotrupes bajulus, Agelastica alni, Leptinotarsa decemlineata, Phaedon cochleariae, Diabrotica spp., Psylliodes chrysocephala, Epilachna varivestis, Atomaria spp., Oryzaephilus surinamensis, Anthonomus spp., Sitophilus spp., Otiorrhynchus sulcatus, Cosmopolites sordidus, Ceuthorrhynchus assimillis, Hypera postica, Dermestes spp., Trogoderma spp., Anthrenus spp., Attagenus spp., Lyctus spp., Meligethes aeneus, Ptinus spp., Niptus hololeucus, Gibbium psylloides, Tribolium spp., Tenebrio molitor, Agriotes spp., Conoderus spp., Melolontha melolontha, Amphimallon solstitialis and Costelytra zealandica. Those belonging to the order of the Hymenoptera, for example, Diprion spp., Hoplocampa spp., Lasius spp., Monomorium pharaonis and Vespa spp. Those belonging to the order of the Diptera, for example, Aedes spp., Anopheles spp., Culex spp., Drosophila melanogaster, Musca spp., Fannia spp., Calliphoro erythrocephala,

Lucilia spp., Chrysomya spp., Cuterebra spp., Gastrophilus spp., Hyppobosca spp., Stomoxys spp., Oestrus spp., Hypoderma spp., Tabanus spp., Tannia spp., Bibio hortulanus, Oscinella frit, Phorbia spp., Pegomyia hyoscyami, Ceratitis capitata, Dacus oleae and Tipula paludosa. Those belonging to the order of the Siphonaptera, for example, Xenopsylla cheopis and Ceratopyllus spp.

The active compounds according to the invention are distinguished by a strong insecticidal activity. They can be used particularly successfully against insects which damage plants, for example, against the larvae of the mustard beetle (Phaedon cochleariae).

In addition, the active compounds according to the invention are suitable for combating soil insects and can be used, for example, for combating the larvae (Pharbia autiqua) of the onion fly.

Also, in addition, the active compounds according to the invention have a strong activity against hygiene and stored-product pests.

The present active compounds can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, wettable powders, granules, aerosols, natural and synthetic materials impregnated with active compound, very fine capsules in

polymeric substances and in coating compositions for seed, and formulations used for burning equipment, such as fumigating cartridges, fumigating cans, fumigating coils and the like, as well as ULV cold mist and warm mist formulations.

These formulations are produced in known manner, for example by mixing the active compounds with extenders, that is, liquid solvents, and/or solid carriers, optionally with surface-active agents, that is emulsifying agents and/or dispersing agents, and/or foam-forming agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents. As liquid solvents, there are suitable mainly aromatic hydrocarbons, such as xylene, toluene or alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane, or paraffins such as mineral oil fractions, mineral oils and vegetable oils, alcohols, such as butanol or glycol as well as their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulfoxide, as well as water; liquefied gaseous extenders or carriers mean liquids which are gaseous at normal

temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocarbons as well as butane, propane, nitrogen and carbon dioxide; as solid carriers, there are suitable, for example, ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly dispersed silicic acid, alumina and silicates; as solid carriers for granules there are suitable, for example, crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, corn cobs and tobacco stalks; as emulsifying and/or foam-forming agents there are suitable, for example, non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulfonates, alkyl sulfates, aryl sulfonates as well as albumin hydrolysis products; as dispersing agents there are suitable, for example, lignin-sulfite waste liquors and methyl cellulose.

Adhesives such as carboxymethyl cellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids,

such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Furthermore, additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally contain between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90% by weight.

The active compounds according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilizing agents, acaricides, nematicides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas and substances produced by microorganisms.

The active compounds according to the invention can further be present in their commercially available formulations and in the use forms, prepared from these

formulations, as a mixture with synergistic agents. Synergistic agents are compounds which increase the action of the active compounds, though it is not necessary that the synergistic agent added is active itself.

The active compound content in the use forms prepared from the commercially available formulations can vary within a wide range. The active compound content in the use forms can be from 0.0000001 to 95% by weight, preferably between 0.0001 and 1% by weight.

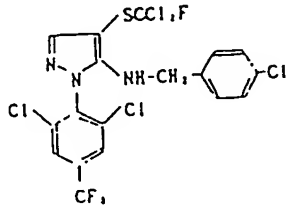
The compounds are employed in a usual manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and soil as well as a good stability to alkali on limed substances.

The biological potency of the compounds according to the invention may be illustrated with reference to the following examples.

Production Example

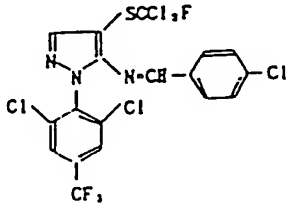
Example 1



To 5.5 g (0.01 mol) of 5-(4-chloro-benzylideneimino)-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-dichlorofluoromethylthio-pyrazole in 100 ml of methanol was added 0.2 g (0.005 mol) of sodium borohydride. The mixture was stirred at room temperature for 16 hours and was evaporated in a vacuum. The residue was collected into dichloromethane, washed twice with water, dried over sodium sulfate, and concentrated in a vacuum. The residue was crystallized by triturating it together with petroleum ether, and the crystals were collected by suction filtration and dried in the air.

There was obtained 5.1 g (93% of theoretical value) of 5-(4-chlorobenzyl-amino)-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-dichlorofluoromethylthiopyrazole having a melting point of 99°C.

Production of Starting Compound

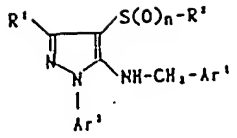


On a water separator was heated 8.6 g (0.02 mol) of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-dichlorofluoromethylthiopyrazole in 200 ml of anhydrous

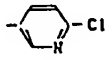
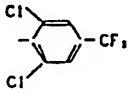
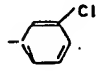
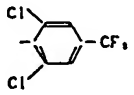
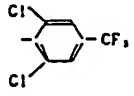
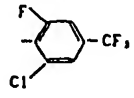
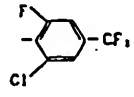
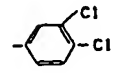
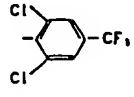
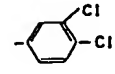
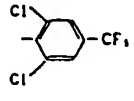
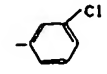
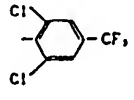
toluene under reflux for 4 hours. Then, 4 drops of concentrated sulfuric acid was added thereto and 8.5 g (0.06 mol) of freshly distilled 4-chlorobenzaldehyde was added dropwise over a period of 2 hours. After the completion of the addition, the mixture was heated at the reflux temperature for further 16 hours, while water freed during the period was separated by means of the water separator. For a treatment, the cooled reaction mixture was washed three times with 100 ml each of saturated sodium hydrogen carbonate solution, dried over sodium sulfate, and then concentrated in a vacuum. The residue was purified by a column chromatography (silica gel; eluent: petroleum ether/ethyl acetate 9:1).

There was obtained 8.5 g (77% of theoretical value) of 5-(4-chlorobenzylideneimino)-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-dichlorofluoromethylthiopyrazole having a melting point of 95°C.

In accordance with the corresponding method and general indications for the production, the following 1-arylpyrazoles of the formula (I) were obtained:

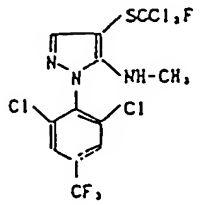


(I)

Example No.	R^1	$-S(O)_n-R^2$	Ar^1	Ar^2	Physical property
2	H	$-SCF_3$			m.p. 103°C
3	H	$-SCCl_2F$			m.p. 93°C
4	H	$-SCCl_2F$			m.p. 138°C
5	CH_3	$-SCF_3$			m.p. 86-87°C
6	CH_3	$-S(=O)CF_3$			m.p. 96-97°C
7	CH_3	$-SCF_3$			m.p. 94-95°C
8	CH_3	$-SCCl_2F$			m.p. 105-106°C
9	CH_3	$-SCCl_2F$			m.p. 109-110°C

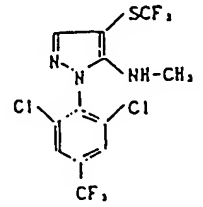
Use Example

In the following Use Example, the following compounds were used as comparative substances:



(A)

5-(N-methylamino)-1-(2,6-dichloro-4-trifluoromethyl-phenyl)-4-dichlorofluoromethylthiopyrazole



(B)

5-(N-methylamino)-1-(2,6-dichloro-4-trifluoromethyl-phenyl)-4-trifluoromethylthiopyrazole

(Both compounds are known in European Patent No. 201,852)

Example A

Phaedon Larvae Test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of an active compound, 1 part by weight of the active compound was

mixed with the above amount of solvent and the above amount of emulsifier, and the concentrate was diluted with water to the desired concentration.

Cabbage leaves (Brassica oleracea) were treated by being dipped into the preparation of the active compound of the desired concentration and were infested with mustard beetle larvae (Phaedon cochleariae), as long as the leaves are still moist.

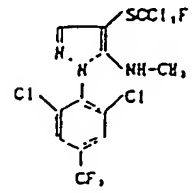
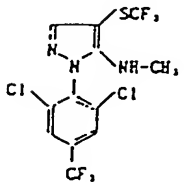
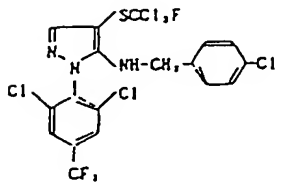
After a predetermined periods of time, the destruction in % was determined. 100% means that all the beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

In this test, the following compound of Production Example, for example, exhibits a superior activity as compared with the conventional compounds.

Table A

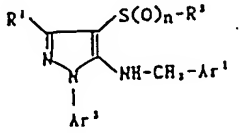
(Plant Pests)

Phaedon Larvae Test

Active compound	Concentration of active Compound (%)	Destruction after 3 hours (%)
 (A) (known)	0.0001	100
	0.00001	10
 (B) (known)	0.0001	100
	0.00001	0
 (1)	0.0001	100
	0.00001	70

The main characteristics and embodiments of the invention are as follows.

1. A substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



(I)

wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,
Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,
Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and
n represents one number of 0, 1 or 2.

2. A substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I) described in the above 1, wherein R^1 represents hydrogen or, in each case, linear or branched alkyl or halogenoalkyl, in each case, having 1 to 4 carbon atoms and, if appropriate, 1 to 9, the same or different, halogen atoms; R^2 represents linear or branched alkyl having 1 to 8 carbon atoms, linear or branched halogenoalkyl having 1 to 8 carbon atoms and 1 to 17, the same or different, halogen atoms, or phenylalkyl or phenyl having, if appropriate, 1 to 4 carbon atoms in the linear

or branched alkyl part and optionally monosubstituted or polysubstituted with the same or different substituent(s), wherein, in each case, appropriate substituents in the phenyl part include halogen, cyano, nitro, or, in each case, a linear or branched alkyl, alkoxy, alkylthio, alkylsulfinyl, alkylsulfonyl, halogenoalkyl, halogenoalkoxy, halogenoalkylthio, halogenoalkylsulfinyl or halogenoalkylsulfonyl, in each case, having 1 to 4 carbon atoms and, if appropriate, 1 to 9, the same or different, halogen atoms in the individual alkyl part; Ar^1 represents phenyl monosubstituted or polysubstituted with the same or different substituent(s), or heteroaryl having 1 to 9 carbon atoms and hetero atom(s), especially 1 to 3 nitrogens, oxygens or sulfurs and optionally monosubstituted or polysubstituted with the same or different substituent(s), wherein appropriate substituents in each case include phenyl substituents as described for R^2; Ar^2 represents phenyl, 2-pyridyl, 3-pyridyl or 4-pyridyl, in each case, optionally monosubstituted or polysubstituted with the same or different substituent(s), wherein appropriate substituents in each case include cyano, nitro, halogen, or, in each case, linear or branched alkyl, alkoxy, or alkoxycarbonyl, in each case, having 1 to 4 carbon atoms, or, in each case, linear or branched halogenoalkyl or halogenoalkoxy, in each case,

having 1 to 9 carbon atoms and 1 to 9, the same or different, halogen atoms, or a group $-S(O)_p-R^3$, wherein R^3 represents amino or, in each case, alkyl, alkylamino, dialkylamino or halogenoalkyl, in each case, having 1 to 4 carbon atoms in the individual alkyl part and, in the case of halogenoalkyl, having 1 to 9, the same or different, halogen atoms; p represents one number of 0, 1 or 2; and n represents one number of 0, 1 or 2.

3. A substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I) described in the above 1, wherein R^1 represents hydrogen, methyl, ethyl, n- or i-propyl or trifluoromethyl, R^2 represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n- or i-pentyl, n- or i-hexyl, chloromethyl, difluoromethyl, difluorochloromethyl, fluorodichloromethyl, trifluoromethyl, pentafluoroethyl, pentachloroethyl, fluorotetrachloroethyl, difluorotrichloroethyl, trifluorodichloroethyl, tetrafluorochloroethyl, heptafluoropropyl, chloroethyl, bromoethyl, chloropropyl, bromopropyl, dichloromethyl, chlorofluoromethyl, trichloromethyl, trifluoroethyl, trifluorochloroethyl, tetrafluoroethyl, difluorochloroethyl, fluorodibromoethyl, difluorobromoethyl, fluorochlorobromomethyl, or phenyl, benzyl or phenylethyl, in each case, optionally monosubstituted, disubstituted or trisubstituted with the

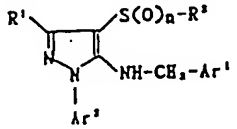
same or different substituent(s), wherein appropriate substituents on phenyl in each case include fluoro, chloro, bromo, iodo, cyano, nitro, methyl, ethyl, methoxy, methylthio, trifluoromethyl, methylsulfinyl, methylsulfonyl, trifluoromethoxy, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl; Ar^1 represents phenyl monosubstituted, disubstituted or trisubstituted with the same or different substituent(s) or pyridyl, furyl or thienyl, in each case, optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents in each case include the phenyl substituents described for R^2; Ar^2 represents phenyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s) or 2-pyridyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents in each case include cyano, nitro, fluoro, chloro, bromo, iodo, methyl, ethyl, n- and i-propyl, n-, i-, s- and t-butyl, methoxy, ethoxy, methoxycarbonyl, ethoxycarbonyl, trifluoromethyl, trichloromethyl, dichlorofluoromethyl, difluorochloromethyl, chloromethyl, dichloromethyl, difluoromethyl, pentafluoroethyl, tetrafluoroethyl, trifluorochloroethyl, trifluoroethyl, difluorodichloroethyl, trifluorodichloroethyl,

pentachloroethyl, trifluoromethoxy, trichloromethoxy, dichlorofluoromethoxy, difluorochloromethoxy, chloromethoxy, dichloromethoxy, difluoromethoxy, pentafluoroethoxy, tetrafluoroethoxy, trifluorochloroethoxy, trifluoroethoxy, difluorodichloroethoxy, trifluorodichloroethoxy, pentachloroethoxy or a group $-S(O)_p-R^3$, wherein R^3 represents amino, methylamino, ethylamino, dimethylamino, diethylamino, fluorodichloromethyl, difluoromethyl, tetrafluoroethyl, trifluorochloroethyl, trichloromethyl, trichloroethyl, trifluoromethyl, methyl or ethyl; p represents one number of 0, 1 or 2; and n represents one number of 0, 1 or 2.

4. A substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I) described in the above 1, wherein R^1 represents hydrogen or methyl; R^2 represents methyl, ethyl, trifluoromethyl, dichlorofluoromethyl or chlorodifluoromethyl; Ar^1 represents phenyl or pyridyl optionally monosubstituted, disubstituted or trisubstituted with the same or different substituent(s), wherein appropriate substituents include fluoro, chloro, bromo, methyl or trifluoromethyl; Ar^2 represents phenyl optionally monosubstituted to pentasubstituted with the same or different substituent(s), wherein appropriate substituents include fluoro, chloro,

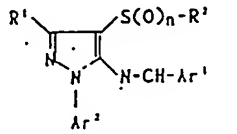
bromo, methyl, ethyl, methoxy, ethoxy, trifluoromethyl, trifluoromethoxy, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl and n represents one number of 0, 1 or 2.

5. A process for producing a substituted 1-aryl-5-(het)arylmethylaminopyrazole of the general formula (I):



(I)

wherein R^1 represents hydrogen, alkyl, or halogenoalkyl,
R^2 represents alkyl, halogenoalkyl, aralkyl which may be optionally substituted, or aryl which may be optionally substituted,
Ar^1 represents substituted aryl or heteroaryl which may be optionally substituted,
Ar^2 represents phenyl or pyridyl which may be, in each case, optionally substituted, and
n represents one number of 0, 1 or 2, wherein a 5-aralkylideneimino-1-arylpyrazole of the formula (II):



(II)

wherein R^1, R^2, Ar^1, Ar^2 and n have the above-described meanings,

is reacted with a reducing agent, if appropriate, in the presence of a diluent.

6. A pest-combating agent comprising at least one substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I).

7. An insecticide comprising at least one substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I).

8. A method for combating an animal pest, wherein the animal pest and/or environment thereof is treated with the substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I).

9. A use of a substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I) at combating an animal pest, especially an insect.

10. A process for producing an animal pest-combating agent wherein a substituted 1-aryl-5-(het)arylmethylaminopyrazole of the formula (I) is mixed with an extender and/or a surfactant.

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Continuation from page 1

(51) Int.Cl.[4]	Identification No.	Reference No. in office
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